

Fine Limestone Additions to Regulate Setting in High Volume Fly Ash Mixtures

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Abstract

High volume fly ash (HVFA) concrete mixtures are being considered more frequently due to their cost and sustainability advantages. While the long term performance of these HVFA concretes typically meets or exceeds that of conventional concretes, their early age performance is often characterized by excessive retardation of the hydration reactions, delayed setting times, and low strengths. Extending an HVFA mixture to a ternary blend that incorporates a fine limestone powder may provide a viable solution to these deficiencies, particularly the hydration retardation and setting issues. In this paper, a nano-limestone powder and two other limestone fillers of increasing median particle size (4.4 μm and 16.4 μm) are investigated for their propensity to accelerate early age reactions and reduce setting times in a Class C fly ash/cement blend. The fineness of the limestone has measurable effects on its efficacy in accelerating hydration and decreasing setting times. Companion specimens prepared with a fine silica powder suggest that the fine limestone may act favorably through both a physical and a chemical mechanism. Isothermal calorimetry and Vicat needle penetration measurements on pastes are accompanied by strength measurements on mortars, to verify that the limestone powder substitutions are not negatively impacting strength development. A linear relationship with a reasonable correlation is found to exist between 1 d and 7 d compressive strengths of mortars and their accompanying cumulative heat release values as determined using isothermal calorimetry.

Keywords: Blended cement; high volume fly ash; isothermal calorimetry; limestone; particle size; setting; strength; ternary blend.

Introduction

As part of the sustainability movement, renewed focus is being placed on mixtures of cementitious materials with a large replacement of cement by supplementary cementitious materials (SCMs), such as high volume fly ash (HVFA) mixtures [1]. While HVFA mixtures can exhibit superior long term strengths and durability in comparison to pure ordinary portland

cement mixtures, they also often exhibit problems with respect to retardation, delayed setting times, and low early age strengths [2-4], thus creating a gap between sustainability and constructability [5]. The delays in setting can be caused both by the retardation of the cement hydration reactions due to interactions with the fly ash and by the inherent reduction in cement content produced by the fly ash substitution, with the fly ash typically being much less reactive than cement at early ages. Previously, powder additions consisting of either calcium hydroxide or a rapid set cement have shown promise in reducing retardation and restoring setting times [2-4]. More recently, the synergistic nature of limestone powder additions to fly ash/cement blends has been explored by research groups in Canada [6] and Norway [7,8]. In the study of Sato and Beaudoin [6], it was clearly demonstrated via isothermal calorimetry and other measurements that a nano-limestone addition significantly accelerated the early age reactions in a blended cement system containing a Class F fly ash, as the blended system without limestone exhibited significant retardation relative to the 100 % ordinary portland cement control. Using a coarser limestone with a median particle size of about 5 μm , De Weerd et al. [8] did not observe an acceleration of the early age reactions in a blended cement containing a Class F fly ash, once again based on isothermal calorimeter curves. In their case, the Class F fly ash itself caused little if any retardation in the blended system. They did however observe a strength enhancement [7], particularly at later ages of 90 d and 180 d, when the limestone replaced either the fly ash or the cement in a blend at a 5 % level by mass.

Neither of these groups reported data on setting times of their respective limestone-fly ash-cement ternary systems. In a previous study, a limestone powder with a median diameter of 16 μm was ineffective in reducing retardation, when added at a 5 % level (mass of total solids) to a Class C fly ash/cement blend [2], in agreement with the observations of De Weerd et al. for their 5 μm limestone [8]. Conversely, the significant acceleration provided by the nano-limestone [6] would suggest a favorable reduction of setting times for pastes prepared with a nano-limestone addition. Therefore, the purposes of the present study were to verify the efficacy of nano-limestone additions in reducing setting time and to examine one or more limestone powders with particle sizes between nano-size and 5 μm . The latter will assist in determining just how fine a limestone powder addition must be to have significant acceleratory effects on early age reactions and to produce a concurrent beneficial reduction in setting time. Consistent with the purposes of this study, a Class C fly ash with known retardation issues was employed. Setting time and isothermal calorimetry curves for pastes were supplemented by measurement of early and later age compressive strengths of mortar cubes, to assure that no detrimental effects on strength were produced.

Materials and Experimental Methods

An ordinary portland cement (ASTM C150 Type I/II [9]) was used in this study, with a Blaine fineness of 476 m^2/kg , a density of 3180 kg/m^3 , an estimated Bogue potential phase composition of 52 % C_3S , 18 % C_2S , 8 % C_3A , and 9 % C_4AF by mass, and a Na_2O equivalent of 0.5 % [10]. A Class C fly ash (ASTM C618-08a [11]) was employed, with a density of 2650 kg/m^3 . Its detailed chemical composition is provided elsewhere [10], but it contained major oxides of 38.7 % SiO_2 , 19.2 % Al_2O_3 , 6.5 % Fe_2O_3 , and 23.5 % CaO by mass. The particle size distributions (PSDs) of the cement and fly ash are provided in Figure 1. Three limestone powders, one a nano-limestone (designated by n) and the other two having median

particle diameters of 4.4 μm (c) and 16.4 μm (o), respectively, were obtained from their manufacturers. The density of each limestone powder is 2700 kg/m^3 . In addition, a finely ground silica with a density of 2650 kg/m^3 and a median particle diameter of 2.7 μm (designated by s) was also investigated as a fine particle activator. The measured PSDs of these four materials, as determined by laser diffraction, are provided in Figure 2. It is recognized that the measurement of the PSD of the nano-limestone powder in this manner is severely limited by the agglomeration of the nano-sized particles and that the individual particles are likely much smaller than the sizes indicated by the curve in Figure 2. Previously, microscopy techniques have been employed to determine that the “true” particle sizes of this nano-limestone are in the range of 50 nm to 120 nm [6]. Following a dispersion technique developed by Sato et al. [12], laser diffraction has yielded a somewhat finer PSD than shown in Figure 2, with a median particle diameter of 180 nm. With the exception of the coarsest of the limestone powders, the fillers are generally significantly finer than either the cement or the fly ash.

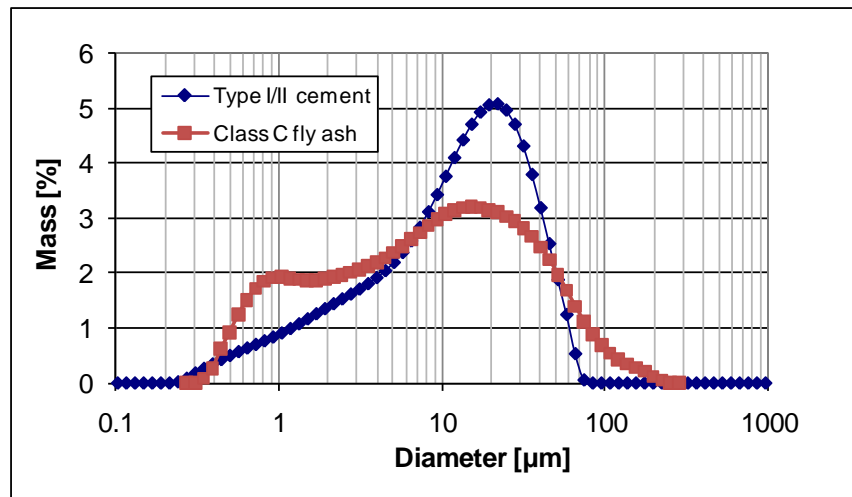


Figure 1. Measured particle size distributions for the cement and fly ash investigated in the study. Results are the average of six individual measurements and error bars (one standard deviation) would fall within the size of the symbols.

For the fairest comparison of setting times and compressive strengths, cement pastes (and the paste fraction of the mortars) were prepared with constant volume fractions of water and powders, based on a control mixture with a water-to-cement ratio by mass (w/c) of 0.30. This low w/c (or w/cm for the mixtures with fly ash) was chosen to provide sufficient early age strength in the HVFA mixtures [10]. For comparison purposes, a plain cement paste with $w/c=0.42$ by mass was also prepared as being more representative of typical transportation concrete designs [10]. Mixture designs for the nine pastes examined in the present study are provided in Table 1. The mixture names indicate the volume percentages of the three components, cement: fly ash: filler, with the letter following the filler content indicating the specific filler employed (n, c, o, or s). A polycarboxylate-based high range water reducing agent (HRWRA) was used at various dosages in the paste mixtures, with the chosen dosage being based on that required in mortars to provide adequate workability for casting cubes. No HRWRA was necessary in the $w/c=0.42$, 100 % cement mixture. Mixing was performed in a high shear blender following the procedure developed by the Portland Cement Association [13], recently approved by ASTM as ASTM C1738-11 [14]. After mixing, truncated conical

specimens were prepared for evaluation of setting times using the Vicat needle and small glass vials were loaded with paste for measurement of heat release using isothermal calorimetry.

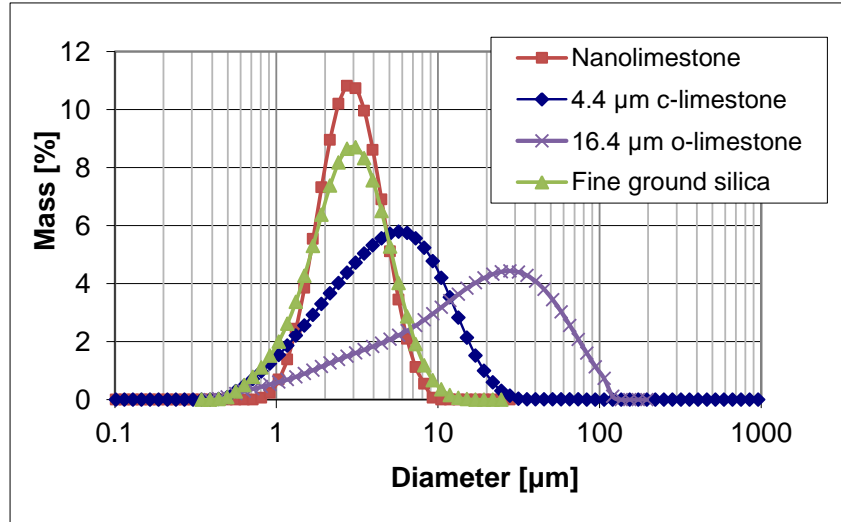


Figure 2. Particle size distributions for the limestone and silica powders investigated in the study.

Table 1. Mixture proportions for cement pastes.

Ingredient/Mixture	100w30	100w42	60:40:0	55:40:5n	55:40:5c	60:35:5c	60:30:10c	60:30:10o	60:35:5s
Cement	400 g	400 g	257.1 g	237.6 g	237.6 g	256.9 g	256.7 g	256.7 g	257.1 g
Fly ash	--	--	142.9 g	144 g	144 g	124.9 g	107 g	107 g	125 g
Nano-limestone	--	--	--	18.3 g	--	--	--	--	--
4.4 μm limestone	--	--	--	--	18.3 g	18.2 g	36.3 g	--	--
16.4 μm limestone	--	--	--	--	--	--	--	36.3 g	--
2.7 μm silica	--	--	--	--	--	--	--	--	17.9 g
Water	120 g	168 g	128.6 g	127.8 g	127.8 g	128.5 g	128.4 g	128.4 g	128.6 g
HRWRA	3.2 g	--	0.68 g	0.22 g	0.22 g	0.24 g	0.34 g	0.34 g	0.24 g
w/cm	0.30	0.42	0.321	0.324	0.324	0.321	0.321	0.321	0.321

The Vicat needle penetration tests were conducted according to the ASTM C191 standard [15], but with the following modification to minimize evaporation from the specimen surface during the test. A moist sponge was held in place in the bottom of a polystyrene foam cup using toothpicks, and the inverted cup placed on top of the truncated conical cement paste specimen, in an effort to maintain a near 100 % relative humidity environment surrounding the hardening cement paste. The cup was removed prior to each measurement and returned immediately after recording the needle penetration. All set time measurements were conducted inside a walk-in environmental chamber maintained at $(25.0 \pm 1.0) ^\circ\text{C}$. In the ASTM C191 standard [15], the single laboratory precisions are listed as 12 min and 20 min for initial and final times of setting, respectively.

Following the general guidelines provided in the ASTM C1702 standard [16], isothermal calorimetry was conducted for a period of at least 1 d using single or replicate paste specimens having a mass of between 5.4 g and 5.6 g. The prepared paste was first placed in the glass calorimeter specimen vials, the vials were sealed, and the sealed vials were then loaded into the calorimeter along with a reference vial containing only dry cement powder. Using this

procedure, the initial “mixing” peak that occurs when water contacts cement was not examined in this study. For this technique, the average absolute difference between replicate specimens of cement paste was previously measured to be 2.4×10^{-5} W/g (cement), with a maximum absolute difference of 0.00011 W/g (cement), for measurements conducted between 1 h and 7 d after mixing [3].

Data for setting times and heat release of the pastes were supplemented by measurements of isothermal calorimetry (for 7 d) and compressive strength (1 d, 7 d, 28 d, and 56 d) on companion mortar mixtures for a subset of the pastes listed in Table 1, also prepared with a constant volume fraction of water and powders. For preparation of the mortars, a blend of four silica sands (density of 2610 kg/m^3) was used, with a constant sand volume fraction of 0.55. Mortars were mixed in a planetary mixer according to ASTM C305-06 procedures [4,17]; cubes were prepared, stored in double sealed plastic bags for 24 h, demolded, and stored in saturated limewater until the age of testing.

Results and Discussion

The investigated cement and fly ash were chosen based on previous results that had indicated a substantial retardation of early hydration and setting for an HVFA mixture [10]. These results are confirmed by the setting and heat flow and cumulative heat release isothermal calorimetry curves shown in Figure 3, Figure 4, and Figure 5, respectively. In Figure 4, the results are normalized per gram of cement powder, while in Figure 5, they are normalized per milliliter of (initial) water. The former focuses attention on the reactivity of the cement, assuming the other powders to be basically inert during the first hours of hydration. The latter examines the heat released per unit volume of capillary porosity; assuming that the volume of created hydration products is proportional to the heat generated, it could potentially relate to the space-filling capabilities of the ongoing reactions (e.g., set and strength development). The initial and final setting times of the various paste mixtures are also summarized in Table 2. The blended paste with 40 % fly ash by volume has an initial setting time that is delayed by over 2 h with respect to the 100 % portland cement control, while its final setting time is likewise delayed by more than 2.5 h. Similarly, in Figure 4, the isothermal calorimetry curve for the 40 % fly ash mixture is shifted to the right by approximately 2.5 h relative to the curve for the 100 % cement, $w/c=0.30$ control, along with the shape of the main hydration peak being somewhat altered.

The two 100 % cement pastes exhibit similar setting times. While one would normally expect a lower w/c paste to exhibit faster setting, in this case, the lower w/c is confounded with the addition of the HRWRA. As can be seen in Figure 4, the isothermal calorimetry curve for the $w/c=0.30$ cement paste with HRWRA is shifted to later times by about 1.5 h with respect to that produced by the $w/c=0.42$ cement paste with no HRWRA addition. From Figure 4 and Figure 5, it is clear that less hydration is required for the setting of the $w/c=0.30$ paste than for the $w/c=0.42$ paste, as would be expected [18]. Thus, the retardation produced by the addition of the HRWRA is offset by the reduction in needed hydration to produce setting for a lower w/c , and in this particular case, the setting times of the two different w/c pastes are basically equivalent.

The results for the nano-limestone powder indicate that a 5 % replacement by volume of cement with the nano-limestone restores the setting times to those of the 100 % cement,

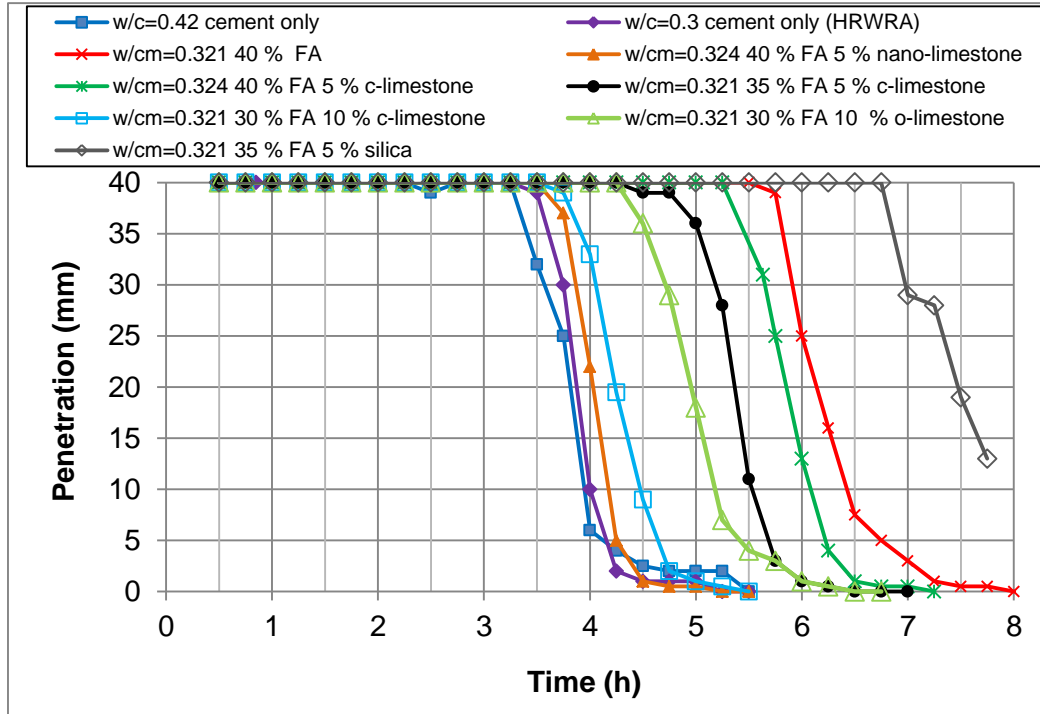


Figure 3. Measured Vicat needle penetrations vs. time for the nine cement pastes.

Table 2. Measured setting times and concurrent heat releases for cement pastes.

Property	100w30	100w42	60:40:0	55:40:5n	55:40:5c	60:35:5c	60:30:10c	60:30:10o	60:35:5s
Initial set time	3.81 h	3.75 h	6 h	3.95 h	5.75 h	5.29 h	4.15 h	4.84 h	7.33 h
Final set time	5.5 h	5.5 h	8.25 h	5.5 h	7.5 h	7 h	5.5 h	7 h	> 7.8 h
Cumulative heat at initial set (J/ml water)	36.4	56.4	40.2	44.7	58.5	51.3	44.3	48.7	48.6
Cumulative heat at final set (J/ml water)	105	124	85	95	111	106	88	118.4	--

$w/c=0.30$ control paste. As has been observed previously [6], the ability of nano-limestone to accelerate the reactions at early ages is clearly indicated in the isothermal calorimetry curves in Figure 4, where the curve with the nano-limestone is shifted more than 3 h to the left with respect to the 40 % fly ash (no limestone) curve. This acceleration in time is also accompanied by an increase in height of the main hydration peak, particularly of the second hump of the peak corresponding to renewed reaction of the aluminates phases [19]. The net effect of these differences, as illustrated by the cumulative heat release curves in Figure 5, is that at an age of 12 h, the heat release in the 5 % nano-limestone paste exceeds that of the 40 % fly ash blend by more than 50 %. As shown in Figure 6, this also resulted in a 12 % increase in the 1 d mortar cube compressive strength, while strengths at later ages were similar in the two systems.

For the particular cement and fly ash combination selected for this study, there is a measurable influence of limestone fineness on early-age performance, as has been observed previously [6]. The first demonstration of this effect can be found in comparing results for the 55:40:5 blends prepared with either the nano-limestone or the 4.4 μm limestone powder, with

equivalent HRWRA dosages. In this case, the much finer nano-limestone produces a significant increase in early age hydration rates and a concurrent decrease in setting times of about 2 h. A similar result is found in comparing the performance of the 60:30:10 blends with either the 4.4 μm or 16.4 μm limestone powders at equivalent HRWRA dosages. Here, the 4.4 μm limestone reduced the setting times back to within the vicinity of the values observed for the control paste, while the setting times exhibited by the paste with the 16.4 μm limestone still exceeded those of the control specimens by an hour or more.

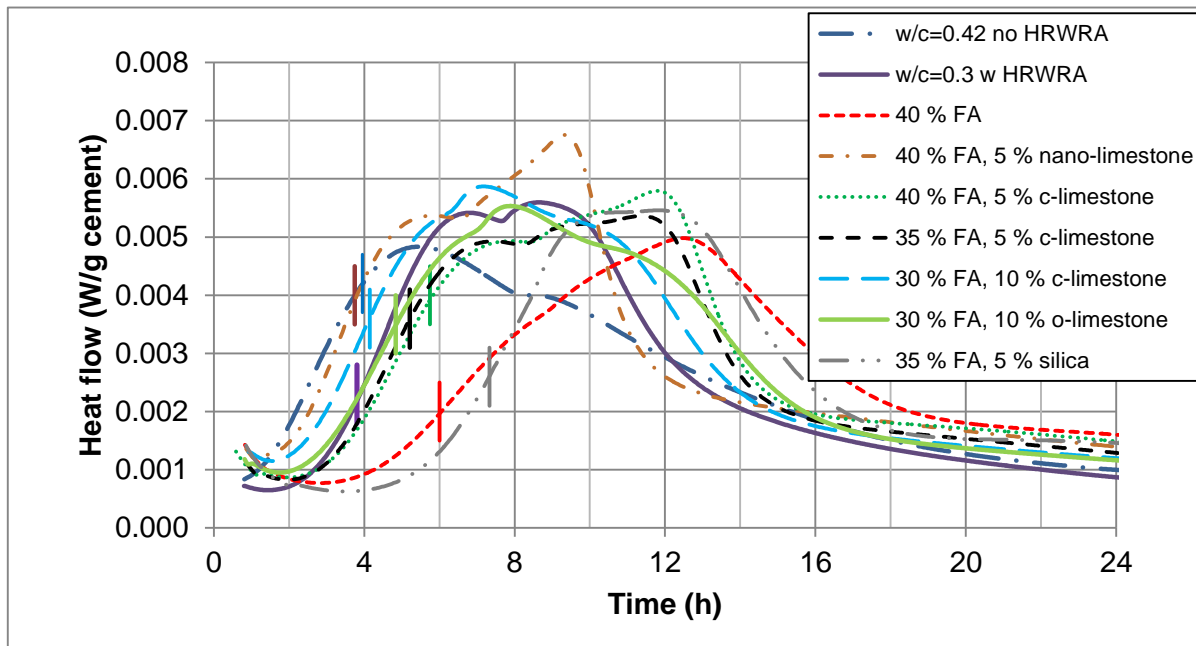


Figure 4. Isothermal calorimetry curves vs. time for the nine cement pastes. For each curve, the short vertical line indicates the initial setting time.

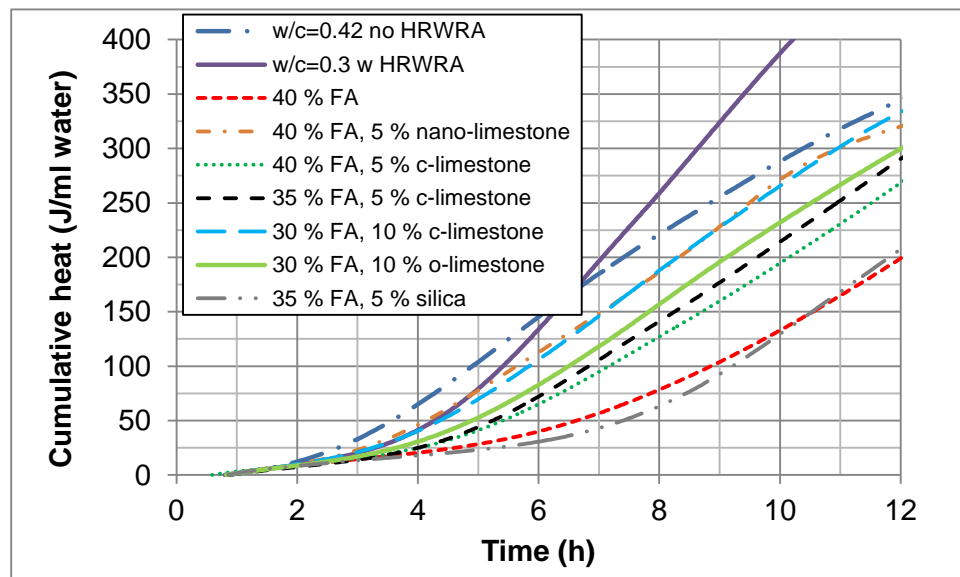


Figure 5. Cumulative heat release curves vs. time for the nine cement pastes on a per milliliter of water basis.

There are at least two mechanisms by which the limestone powder can be influencing the early age behavior of these blended cement pastes. First, the limestone powder can be functioning as a fine filler, providing additional surfaces for the nucleation and growth of hydration products [20,21]. In this case, the greatly increased surface area of the nano-limestone relative to the other two limestones would be expected to accelerate the early age reactions, in agreement with the present results. Second but perhaps less likely, the limestone powder could potentially provide an additional source of calcium ions to the pore solution, even though CaCO_3 has a relatively low solubility at the elevated pH levels that will quickly be encountered in typical cement paste pore solutions. But, it must be recognized that for these specimens, the initial contact always occurs between the pre-blended powders and a circumneutral distilled water (pH near 7), in which the solubility of calcium carbonate will be much higher than in a typical pH~13 pore solution.

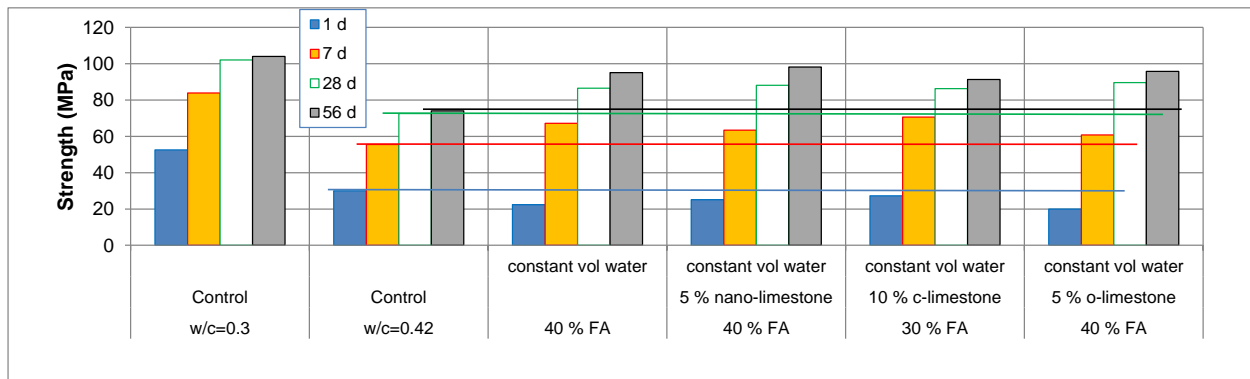


Figure 6. Measured compressive strengths for mortar cubes at four ages. “Constant vol water” indicates that mortar specimens were prepared with constant volume fractions of water, powders, and sand, which were the same as those used in the control $w/c=0.3$ mortar. Average standard deviation in testing three cubes for each mixture at each age was 2.4 MPa.

Some support for this latter mechanism is provided by comparing the results for the 60:35:5 systems prepared with either the $4.4\ \mu\text{m}$ limestone or the $2.7\ \mu\text{m}$ silica, particularly focusing on the isothermal calorimetry curves in Figure 4 and Figure 5. For the silica substitution, the dormant period is actually lengthened relative to that observed for the 40 % fly ash blended cement with no fillers. However, once hydration starts in earnest, the system with the 5 % silica exhibits a higher hydration rate. The lengthening of the dormant period suggests that the silica (certainly not supplying calcium ions to solution) may in fact be decreasing available calcium, as perhaps some of the fine silica is amorphous, as opposed to crystalline, and therefore more reactive in a high pH solution. Conversely, with the limestone powder perhaps supplying calcium ions to the pore solution and certainly providing ample additional surface area for the nucleation and growth of hydration products, the dormant period is decreased and the subsequent hydration is accelerated. Clearly, additional research is needed to isolate and clarify the contributions of these two mechanisms.

These same effects might not be observed at all in a system that is not on the edge of calcium deficiency, as exemplified by the results obtained with limestone and quartz powders (each about $5\ \mu\text{m}$ in diameter) in a Class F fly ash blended cement that were recently presented

in reference [8]. As another example of the influence of the silica powder on early age reactions, isothermal calorimetry results for mortars with various volumetric substitutions for cement by a silica powder (slightly coarser than the one employed in the current study) are provided in Figure 7 [22]. In this case, the three mortars with silica substitutions were prepared with the same dosage of HRWRA, while the HRWRA dosage in the 100 % cement mortar was double this value to provide adequate flow [10]. Focusing on the various silica substitution levels, one finds that in going from 40 % to 60 % silica, the early age hydration is accelerated, while in going from 60 % to 80 %, an increase in the dormant period is observed. However, once hydration begins in earnest, the hydration rates in the 80 % system are similar to those observed for the other two substitution levels. At this highest substitution level, it appears that the silica powder may be finally consuming a sufficient quantity of calcium ions to delay the onset of the primary hydration peak. This hypothesis must be tempered by the facts that the w/c of the 80 % silica mixture is higher than that in any of the other mixtures (which could also provide some contribution to a dilution of pore solution concentrations) and that the HRWRA to cement ratio is also highest in the 80 % silica mixture.

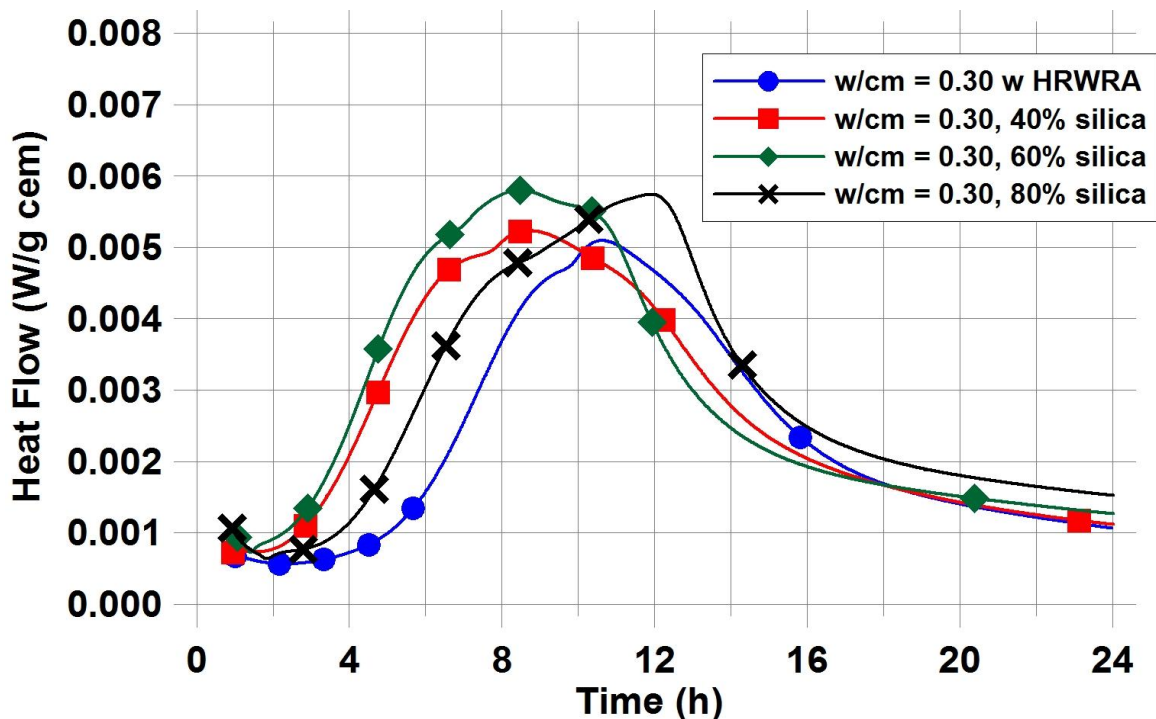


Figure 7. Isothermal calorimetry results for mortars with various volumetric substitutions of silica powder for cement [22].

Mortar cube compressive strengths are provided in Figure 6 for a subset of the mixtures, with their corresponding isothermal calorimetry curves being provided in Figure 8. In general, the trends observed in the mortar calorimetry curves are the same as those obtained for their equivalent pastes in Figure 4. These mortars were prepared to verify that the limestone powder replacements were not having any serious deleterious influences on compressive strengths. In general, the 1 d compressive strengths of the mixtures with limestone exceed that of the 40 % fly ash blended cement paste, with later age strengths being generally comparable, in agreement with the general observations from a previous blended cement study [7]. If the goal of an HVFA

blend is to match the compressive strength of the $w/c=0.42$, 100 % cement mortar, the various mixtures with fly ash or fly ash and limestone exceed this goal at the ages of 7 d, 28 d, and 56 d, but fall somewhat short at an age of 1 d. For the 1 d results, of the subset of mortars that were evaluated, the 60:30:10c system comes the closest to matching the strength of the 100 % cement control. In this case, benefits are obtained from both the 10 % limestone replacement for fly ash and the accompanying reduction of the fly ash content from 40 % to 30 %, as the latter is chiefly responsible for the retardation present in these binary and ternary mixtures. It should be pointed out, though, that this 60:30:10c mixture still obtains a 40 % reduction in cement content relative to a 100 % cement, $w/c=0.30$ mixture, and a 33 % reduction in cement content (volume) relative to its $w/c=0.42$ counterpart, illustrating the potential sustainability benefits of these ternary blends.

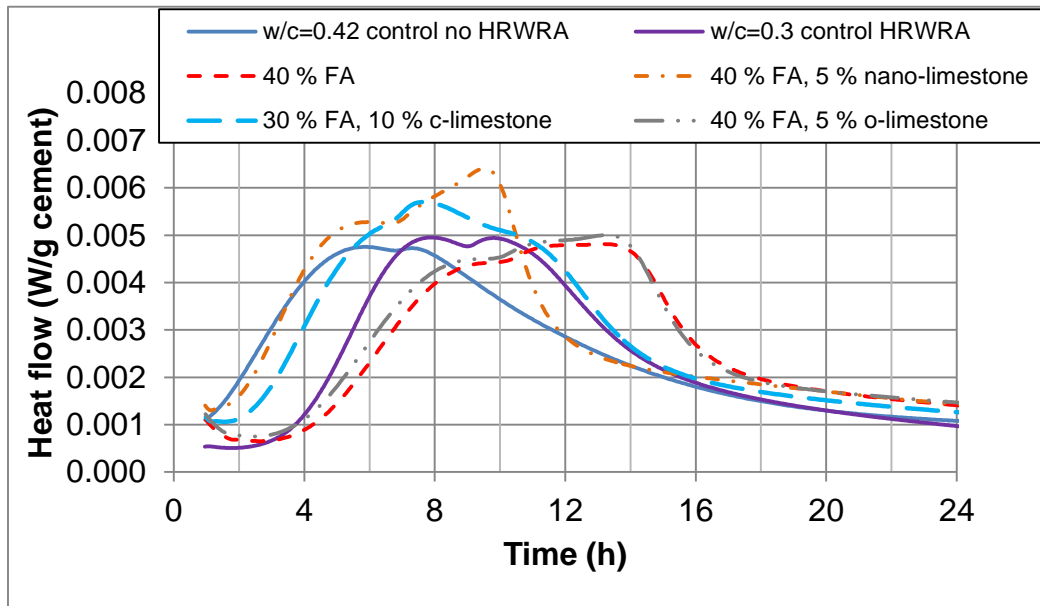


Figure 8. Isothermal calorimetry curves vs. time for the six mortar mixtures.

A further topic to be addressed within the scope of the present experiments is the relationship between isothermal calorimetry and the development of mechanical resistance (setting and strength) for a cement paste or mortar. As mentioned previously, a higher w/c mixture will generally require a greater degree of hydration to achieve setting [18], as observed in the present study (Table 2). However, for a constant volume fraction of water, as employed for eight of the paste mixtures examined in this study, one might expect a reasonable correlation between heat release and setting or strength development [3]. With this in mind, the cumulative heat release values up to the times of initial and final set have been included in Table 2. These cumulative heat release values do not include the contributions from the initial mixing and dissolution of cement phases, as data acquisition typically began 1 h after the initial contact between cement and water. Assuming that most of the heat generation during this first hour is due to the input of mixing energy and dissolution processes, neglecting this contribution when considering a potential relationship between heat release and the formation (precipitation) of hydration products would seem to be a reasonable approach. For the eight paste mixtures with a constant volume fraction of water (and powders), for the cumulative heat release at the times of initial set, an average value of 46.6 J/ml water with a coefficient of variation of 15 % is

determined. The equivalent values for the times of final set are 101.2 J/ml water and 12 %, with one less data point due to the lack of a final setting time determination for the ternary blend with the fine silica powder. These coefficients of variation for cumulative heat release at initial and final set are similar to those found in a previous study for fly ash/cement blends with various powder additions (gypsum, rapid set cement, and calcium hydroxide) [3].

The relationship between cumulative heat release and strength development is explored in Figure 9 that plots the 1 d and the 7 d compressive strengths for the mortar mixtures vs. their cumulative heat release (at the same age) on both a per milliliter of paste and a per milliliter of (initial) water basis. When plotted against the cumulative heat release on a per milliliter paste basis, the results for the $w/c=0.42$ mortar are separated from the others that all contain the same initial volume fraction of water. However, when plotted against the cumulative heat release on a per milliliter of (initial) water basis, all of the results for these mortars are seen to basically lie on a single straight line with some scatter ($R^2=0.972$). This reasonable correlation between early age cumulative heat releases and strengths has been observed previously for portland cements of different finenesses [23], and has also recently been demonstrated for blended cements prepared with a variety of fly ashes and natural pozzolans, when a constant volumetric proportioning paradigm was employed [24].

While the use of fine limestone is effective in accelerating hydration and reducing setting times for HVFA mixtures, it is clear from the present results that much research remains for optimizing binary and ternary blends of HVFA mixtures. Furthermore, while the critical role of the particle size distributions of each constituent component can be inferred from the present results, other recent studies have clearly demonstrated the benefits of other approaches to intentionally engineering these characteristics [25,26]. In a previous study [25], design of experiment has been utilized to optimize a binary HVFA mixture via the blending of a fine cement with a coarse fly ash, to provide equivalent 1 d and 28 d strengths to those of a 100 % portland cement mixture of equivalent water volume fraction, without a dramatic increase in HRWRA requirements. In another study [26], a similar approach has been pursued to produce a gap-graded ternary blend consisting of a fine highly reactive SCM to enhance overall reactivity, an intermediate-sized cement, and a coarse low reactivity SCM material. The results of these two earlier studies, along with those of the current study, exemplify alternative methods to accelerate hydration and reduce the negative early age aspects of using HVFA mixtures. While effective, these approaches represent only a few of the many possibilities for optimizing the performance and sustainability of the complex powder mixtures that will serve as the binder phase of future concretes.

Conclusions

The following conclusions can be drawn from the current study on this particular fly ash/cement combination that had exhibited considerable retardation and delays in setting relative to an equivalent 100 % cement mixture:

- 1) a 5 % replacement of nano-limestone for cement on a volume basis, in addition to accelerating the early age reactions, is also effective in reducing the times of initial and final set,
- 2) the particle sizes of the limestone powders are a key variable influencing their performance as accelerators of reaction and setting; while a nano-limestone is highly efficient in this regard, the

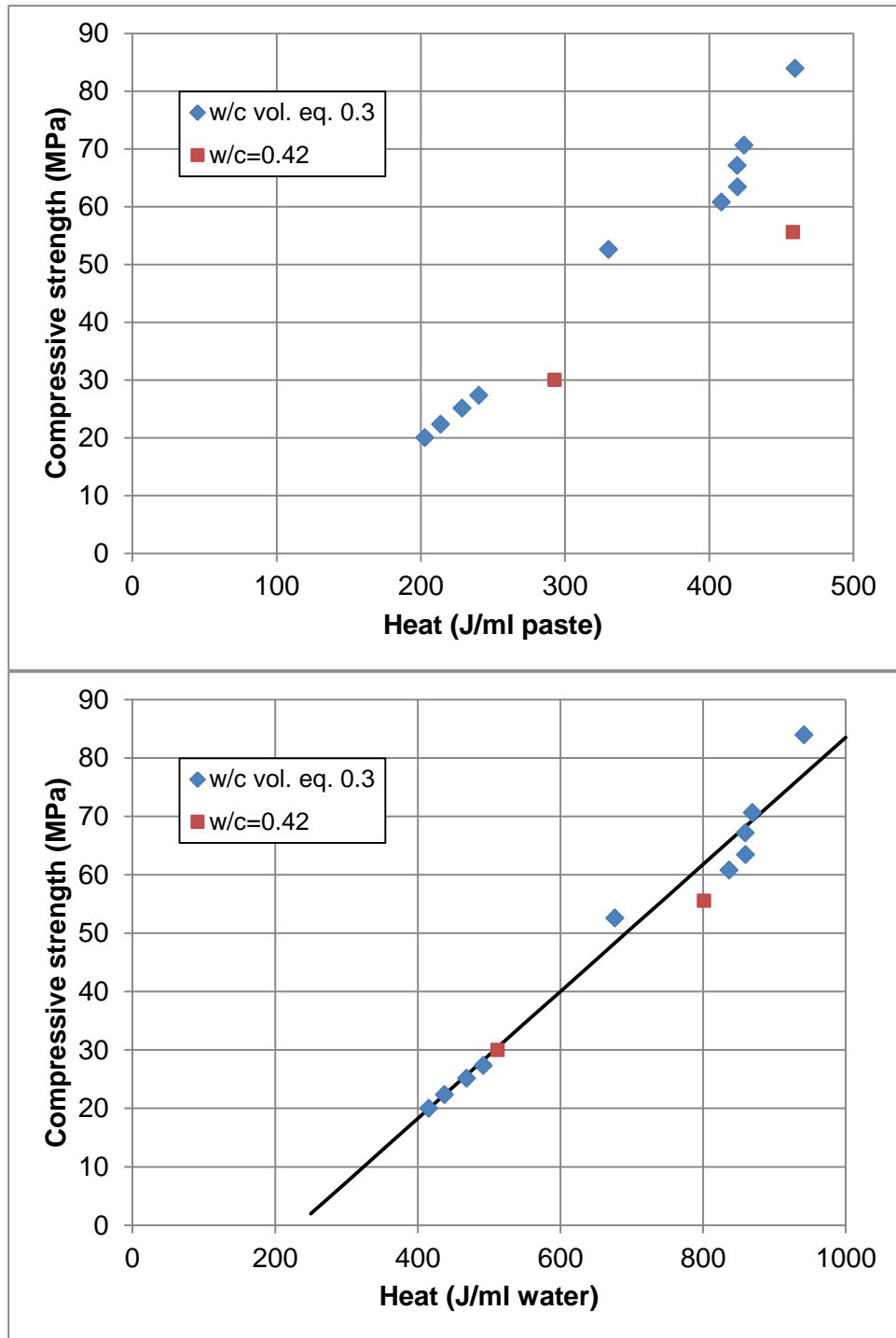


Figure 9. Measured compressive strengths vs. measured cumulative heat release on either a per milliliter paste basis (top) or a per milliliter initial water basis (bottom) for mortars at ages of 1 d and 7 d.

4.4 μm limestone is also effective when used as a 10 % volumetric replacement for the fly ash in a blended cement,

- 3) for a constant volume fraction of water in a paste, a reasonable correlation was exhibited between times of initial and final set and their corresponding cumulative heat releases on a per milliliter water basis,
- 4) for the 1 d and the 7 d compressive strengths of the mortar cubes, a linear relationship with $R^2=0.972$ was observed between strength and cumulative heat release per milliliter (initial) water, for the two volume fractions of water investigated in the present study (corresponding to $w/c=0.42$ and $w/c=0.30$ in the 100 % portland cement controls).

Finally, it should be reiterated that each fly ash/cement/admixture mixture is unique and that the results obtained for the particular set of materials employed in the present study may not hold for other material choices. Still, when retardation and setting time delays are encountered in an HVFA mixture, fine limestone powder replacements may offer a viable remedy to the ready-mix producer and are certainly worthy of consideration as a potential mitigation strategy.

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References

- 1) Mehta PK. Global concrete industry sustainability. *Concr Inter* 2009;31(2):45-48.
- 2) Bentz DP. Powder additions to mitigate retardation in high volume fly ash mixtures. *ACI Mat J* 2010;107(5):508-514.
- 3) Bentz DP, Ferraris CF. Rheology and setting of high volume fly ash mixtures. *Cem Concr Comp* 2010;32(4):265-270.
- 4) Bentz DP, Ferraris CF, De la Varga I, Peltz MA, Winpiger J. Mixture proportioning options for improving high volume fly ash concretes. *Inter J Pavement Res Tech* 2010;3(5):234-240.
- 5) Cost, V.T. Concrete sustainability versus constructability – Closing the gap. 2011 International Concrete Sustainability Conference, Boston, 2011.
- 6) Sato T, Beaudoin J. Effect of nano- CaCO_3 on hydration of cement containing supplementary cementitious materials. *Adv Cem Res* 2011;23(1):1-11.

- 7) De Weerd K, Kjellsen KO, Sellevold E, Justnes H. Synergy between fly ash and limestone powder in ternary cements. *Cem Concr Comp* 2011;33(1):30-38.
- 8) De Weerd K, Ben Haha M, Le Saout G, Kjellsen KO, Justnes H, Lothenbach B. Hydration mechanisms of ternary Portland cements containing limestone powder. *Cem Concr Res* 2011;41:279-291.
- 9) ASTM C150. Standard specification for Portland cement; 2009.
- 10) De la Varga I, Castro J, Bentz D, Weiss J. Internal curing concepts in mixtures containing high volumes of fly ash. to be submitted, 2011.
- 11) ASTM C618-08a. Standard specification for coal fly ash and raw or calcined natural pozzolan for use in concrete; 2008.
- 12) Sato T, Daillo F, Trischuk K. Dispersion of nano- CaCO_3 coated with various surfactants for accelerating hydration of cement. to be submitted, 2011.
- 13) Helmuth RA, Hills LM, Whiting DA, Bhattacharja S. Abnormal concrete performance in the presence of admixtures. 1995 PCA serial # 2006.
- 14) ASTM C1738-11. Standard practice for high-shear mixing of hydraulic cement pastes; 2011.
- 15) ASTM C191-08. Standard test methods for time of setting of hydraulic cement by Vicat needle; 2008.
- 16) ASTM C1702-09a. Standard test method for measurement of heat of hydration of hydraulic cementitious materials using isothermal conduction calorimetry; 2009.
- 17) ASTM C305-06. Standard practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency; 2006.
- 18) Bentz DP, Peltz MA, Winpigler J. Early-age properties of cement-based materials: II. Influence of water-to-cement ratio. *ASCE J Mat Civ Eng* 2009;21(9):512-517.
- 19) Sandberg PJ, Roberts LR. Cement-admixture interactions related to aluminate control. *J ASTM Inter* 2005;2(6):1-14.
- 20) Gutteridge WA, Dalziel JA. Filler cement: The effect of the secondary component on the hydration of portland cement. Part I. A fine non-hydraulic filler. *Cem Concr Res* 1990;20:778-782.
- 21) Bentz DP, Modeling the influence of limestone filler on cement hydration using CEMHYD3D. *Cem Concr Comp* 2006;29(2):124-129.
- 22) De la Varga I. Ph.D. thesis, Purdue University, 2011.

23) Bentz DP, Blending different fineness cements to engineer the properties of cement-based materials. Mag Concr Res 2010;62(5):327-338.

24) Bentz DP, Durán-Herrera A, Galvez-Moreno D. Comparison of ASTM C311 strength activity index testing vs. testing based on constant volumetric proportions. accepted by J ASTM Inter 2011.

25) Bentz DP, Hansen AS, Guynn JM. Optimization of cement and fly ash particles to produce sustainable concretes. Cem Concr Comp, 2011;33(8):824-831.

26) Zhang T, Yu Q, Wei J, Zhang P. A new gap-graded particle size distribution and resulting consequences on properties of blended cement. Cem Concr Comp 2011;33(5):543-550.